PB-213 721

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Environmental Protection Agency
Norton, West Virginia

1972

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Paper Presented at the Fourth Symposium on
Coal Mine Drainage Research, Pittsburgh, Pennsylvania
April 26, 1972

TREATMENT OF FERROUS IRON ACID MINE DRAINAGE BY REVERSE OSMOSIS

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INTRODUCTION

In 1969, Rex Chainbelt under contract to the Commonwealth of Pennsylvania and the Federal Water Quality Administration (now Environmental Protection Agency) studied reverse osmosis treatment of a ferrous iron discharge at Mocanaqua, Pennsylvania.[1] Using a tubular system, a loss of 90 percent of the original product flow in 400 hours of operation due to iron fouling was observed. Though sodium hydrosulfide flushes were successful in flux restoration, fouling immediately recurred upon resumption of operation on the ferrous water.

In other studies using spiral wound reverse osmosis units, Riedinger and Shultz[2] in 1966 and Wilmoth and Scott[3] in 1970 treated ferrous acid mine drainage discharges of similar quality to the Mocanaqua water and observed no severe fouling. No fouling of the extreme nature seen at Mocanaqua was observed in reverse osmosis studies by Gulf Environmental Systems[4] and EPA's Norton Mine Drainage Treatment Field Site on a ferric acid mine drainage.

To investigate the Mocanaqua fouling phenomena, EPA and the Commonwealth of Pennsylvania contracted with Rex Chainbelt to evaluate the iron fouling problem in the laboratory, to modify the tubular system, and to conduct additional studies at Mocanaqua. In order to make these studies more comprehensive, EPA was to conduct simultaneous studies with a spiral wound reverse osmosis unit at the same site. A hollow fiber R.O. permeator was also obtained for this study and EPA later enlarged it to a three permeator array for a hollow fiber system of comparable size to the spiral wound system.

For the ensuing study, all three systems operated side by side on the same water, the only exception to this being acid injection to the feed during the last phase of spiral wound testing. Thus, a unique opportunity was provided for direct comparison of systems and for investigation of the Mocanaqua iron fouling phenomenon.

Typical water quality characteristics of the Mocanaqua discharge are presented in Table 1.

Table 1
Typical Raw Water Quality Characteristics
of Mocanaqua Discharge

		Units
pH	3.4	
Conductance	1100	Mmhos/cm
Acidity	230	mg/l as $CaCO_3$
Calcium	120	mg/l
Magnesium	90	"
Total Iron	80	"
Ferrous Iron	68	"
Aluminum	11	"
Sulfate	800	"
Manganese	15	"
Silica	10	"
TDS	1200	"
Dissolved Oxygen	<1	"
Temperature	54	°Fahrenheit

CONCLUSIONS

The following conclusions were made based on data obtained from this study:

-Under proper operating conditions, reverse osmosis can be used to treat ferrous iron acid mine drainage without major iron and calcium sulfate fouling problems.

-Flux declines observed using optimized flow schemes were tolerable for all three units but the spiral wound and hollow fiber were slightly superior in flux stability.

-Although salt rejections were near 99 percent for all three units, product water would still need further treatment for iron and manganese removal and pH adjustment before potable standards could be met.

-An intolerable flux decline rate was observed for the tubular system when high salt passage (1.5 percent) membranes were utilized, while lower salt passage (0.4 percent) membranes had significantly improved flux stability.

-Oxidation of ferrous iron by bacteria can be inhibited by ultraviolet disinfection and/or by lowering the pH to 2.9 by acid injection.

-Water recovery was limited to slightly above 75 percent due to calcium sulfate precipitation which occurred when brine $CaSO_4$ molar solubility product values were in the range of 35-50 $\times 10^{-5}$.

-No observable loss in membrane salt rejection capability occurred during this six month study.

-The tubular system had significantly lower productivity and higher initial cost as compared to the hollow fiber and spiral wound system in this application.

PROCEDURES

Test Equipment

The spiral wound reverse osmosis system was a Gulf Environmental Systems' 4K unit (nominal 4,000 gallons per day of product flow) which utilized three 4" x 10' steel schedule 40 pressure vessels. Each vessel contained three spiral wound modules with cellulose acetate membranes. A schematic drawing of the spiral configuration is given in Figure 1. Two sets of modules were used during this study. During Phase I, each module contained 50 square feet of standard percholate modified cellulose acetate membrane for a total unit membrane area of 450 square feet. The modules used for Phase II contained 62 square feet of Formamid modified cellulose acetate for a total unit membrane area of 558 square feet. Three modules were placed in series in each tube. There were two effluents from each module, i.e., brine and product water. Typically, the brine from one module (or tube of modules) serves as the feed to the next module (or tube of modules) and is progressively concentrated in this manner. This was the case in the spiral unit where brines from tubes 1 and 2 were combined to serve as the feed for tube 3.

Figure 2 presents the system arrangement and flow diagram for the Gulf unit. Acid mine water was pumped through ten micron cartridge filters and an ultraviolet disinfection light before entering the reverse osmosis unit. UV disinfection was felt necessary in an attempt to inhibit bacteriological oxidation of the ferrous iron which had presumably contributed to fouling observed in earlier studies.[1] A Gould MB 13600* multi-stage centrifugal pump supplied water to the reverse osmosis unit at pressures up to 600 psig. In order to attain high recoveries in the small 4K unit and yet maintain sufficient brine flow velocity and turbulance in each module to prevent 'boundary layer' precipitation, it was necessary to recycle a portion of the brine into the feed to the R.O. unit. In this case, the spiral unit membranes were actually treating the blended feed (mixture of raw water and recycled brine) rather than raw feed. During Phase II, sulfuric acid was injected to lower the blended feed pH to 2.9 and thus inhibit both ferrous oxidation and ferric precipitation.

The hollow fiber system, manufactured by DuPont, initially consisted of one permeator on loan from DuPont to Rex Chainbelt. Fifteen hundred square feet of B-9 hollow fiber nylon membrane were packed in a 6" x 4' stainless steel pressure vessel as illustrated in Figure 3. During Phase I, the single DuPont permeator operated at 400 psi from a Moyno high pressure pump which also supplied feed water to the tubular unit. Phase I DuPont tests were successful so EPA purchased two additional permeators for Phase II and formed a three permeator array, 6K unit, as shown in Figure 4. The brine from both new permeators in parallel served as the feed to permeator number 3 (the original one). Flow control orifices were placed in each brine line from permeators one and two to insure equal brine flows and prevent system unbalance. Because high brine flows are not required for hollow fiber systems, it was not necessary to recycle brine. Therefore, the unit was actually receiving raw acid mine water which had been filtered and had passed through the ultraviolet light for disinfection.

*Mention of commercial products does not imply endorsement by the Environmental Protection Agency.

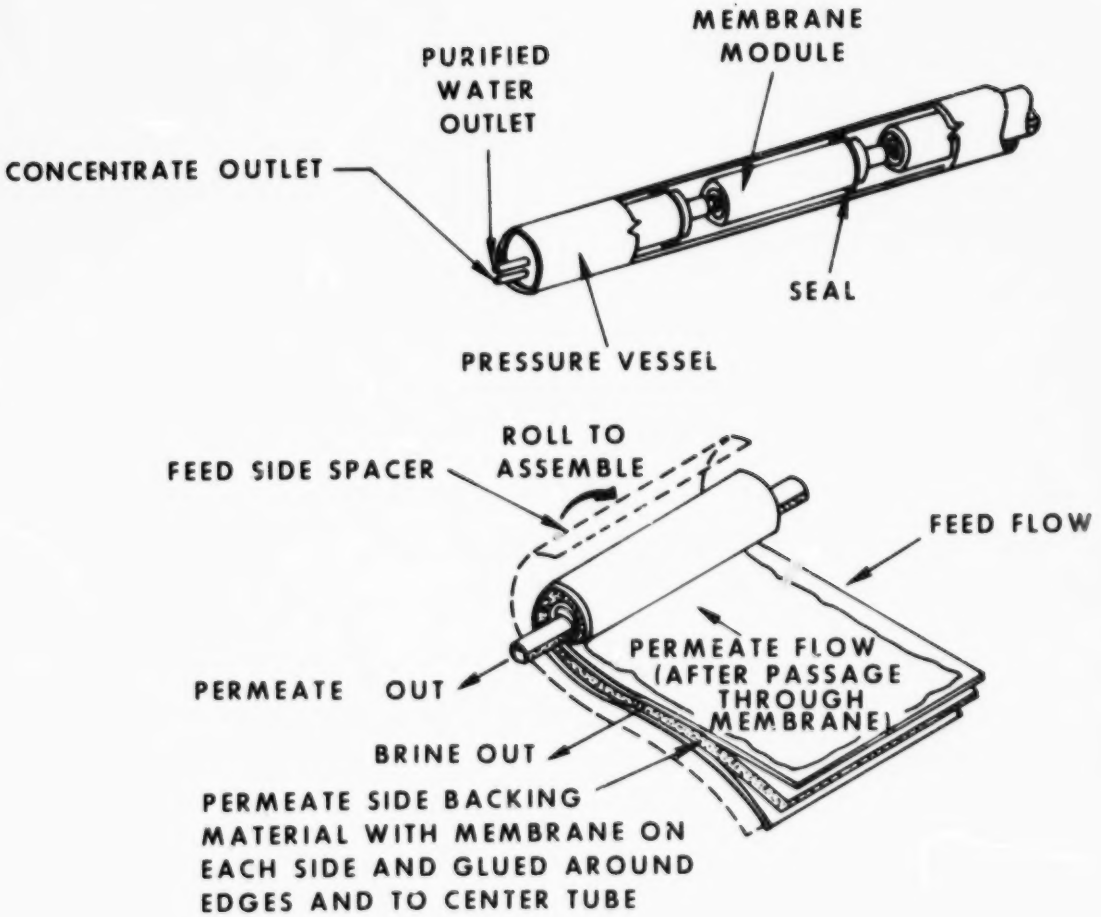
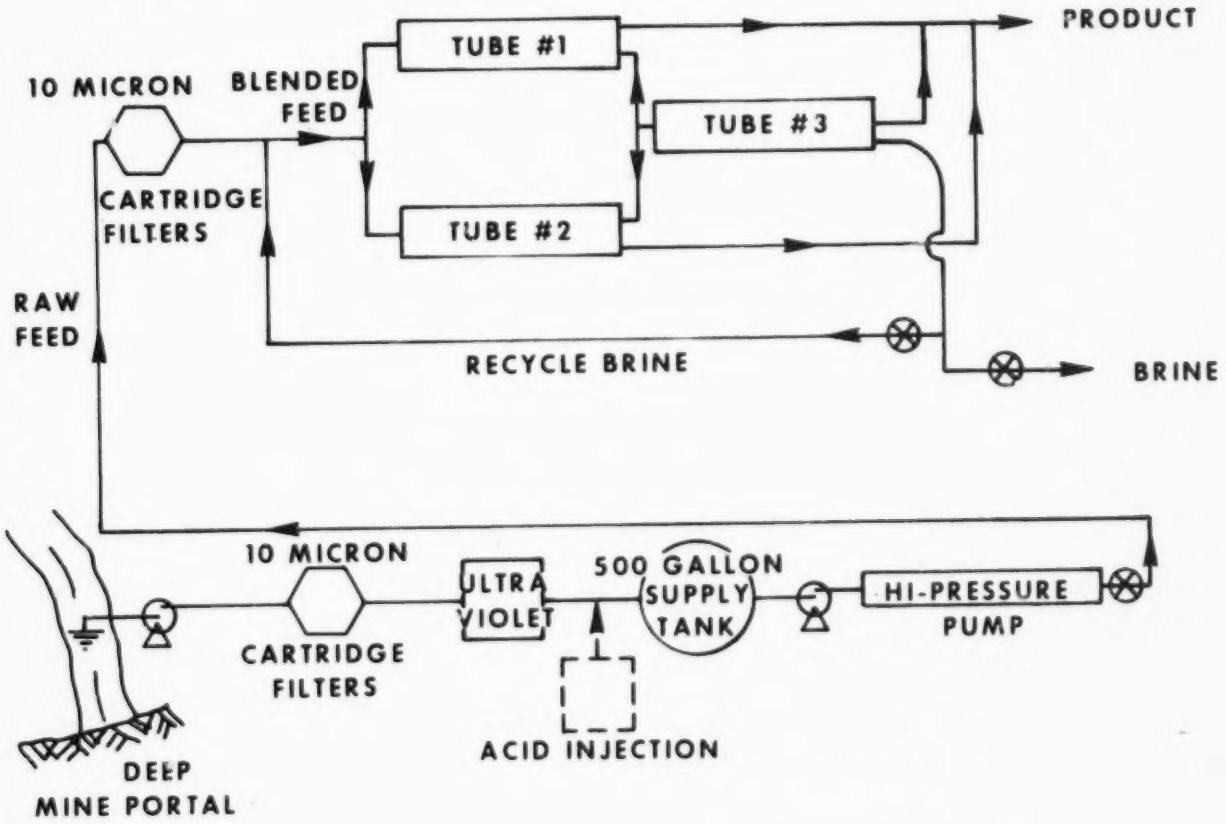


FIGURE 1
SPIRAL WOUND CONFIGURATION

FIGURE 2

SPIRAL WOUND 4K REVERSE OSMOSIS UNIT



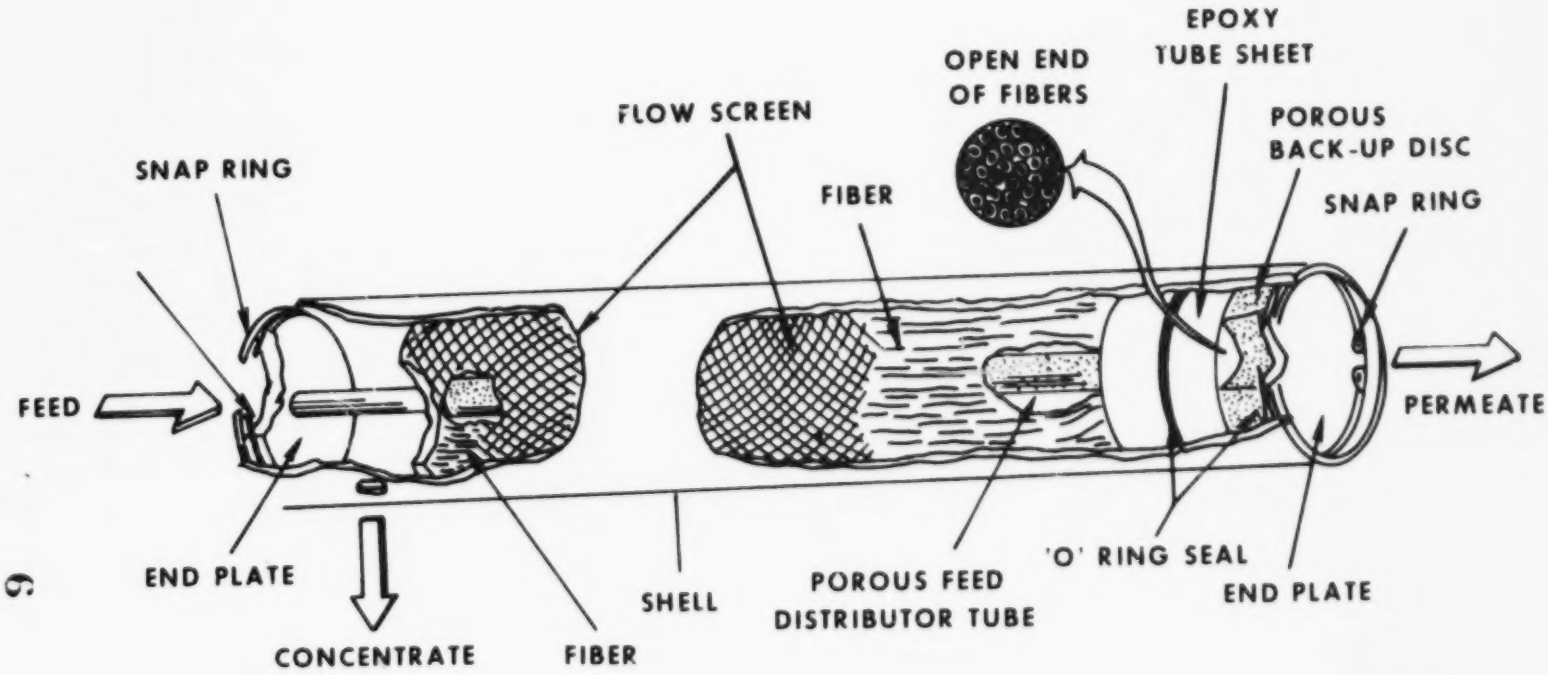
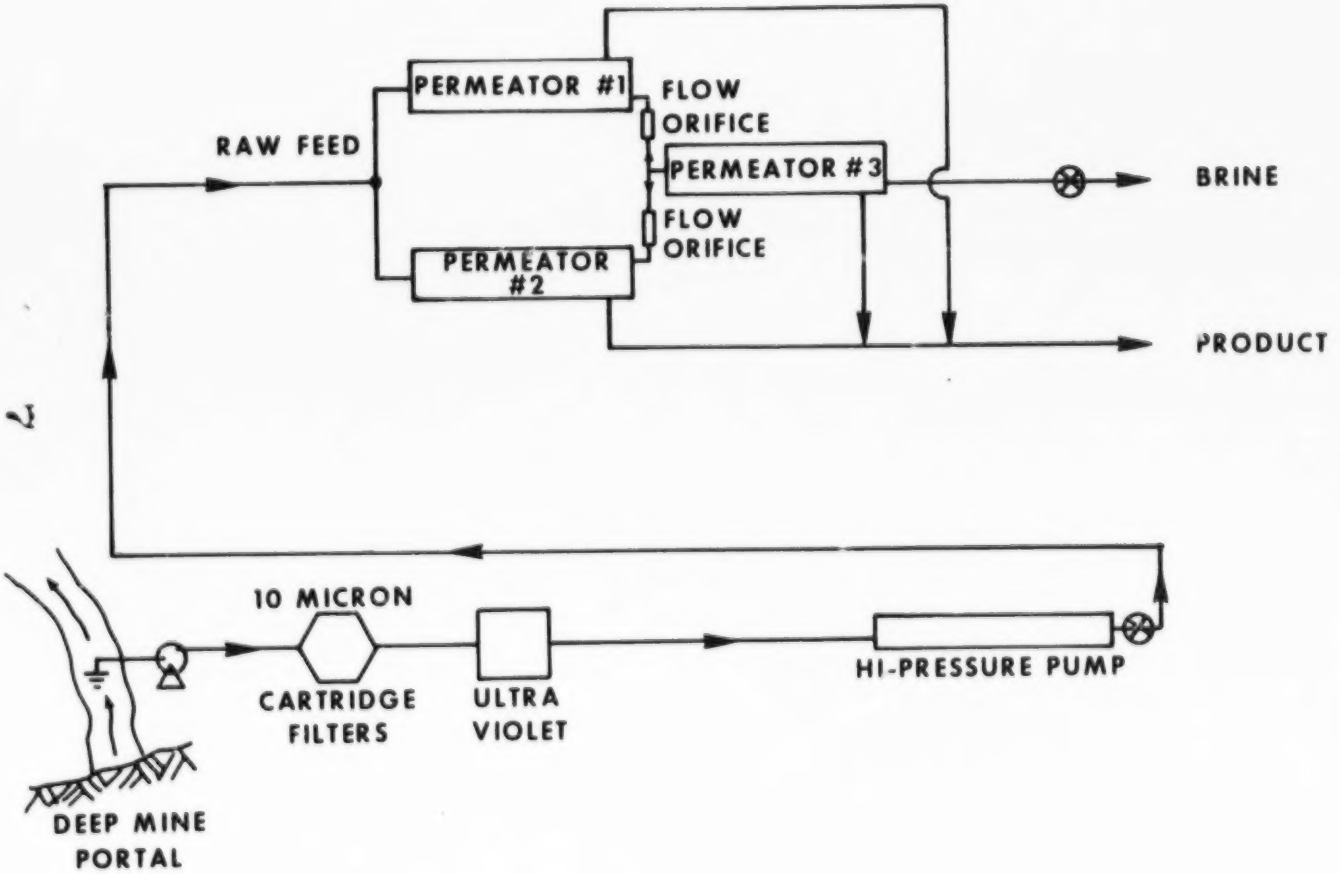


FIGURE 3

HOLLOW FIBER MODULE

FIGURE 4

HOLLOW FIBER 6K REVERSE OSMOSIS UNIT



Phase I tubular studies utilized a unit consisting of 60 3" x 7' 10" plastic tubular #310 modules illustrated in Figure 5 and arranged as shown in Figure 6. The tubular system was manufactured by Calgon-Havens Company. Each module contained eighteen one-half inch i.d. porous fiberglas tubes which were lined with cellulose acetate membrane and connected in series. Membrane area was 16.9 ft^2 per module for a total system membrane area of 1,014 square feet. Pretreatment was the same as that for Phase I Gulf and DuPont, i.e. 10 micron filtration and UV disinfection.

Turbulance promotion rods were placed in modules where brine flow was lowest to inhibit 'boundary layer' precipitation and fouling. Unfortunately, use of turbulence promoters also resulted in high pressure drops across the modules in which they were installed thus reducing the average applied pressure.

During Phase II, the 60 #310 modules were replaced with five #610 modules for a total membrane area of 84.5 ft^2.

Analytical Procedures

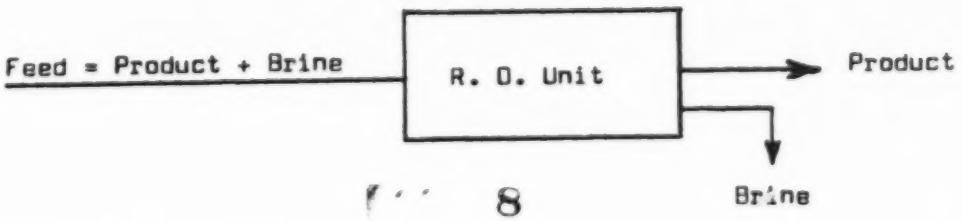
Acidity, ferrous iron, pH, conductivity, and dissolved oxygen determinations were made on site. Acidified samples were returned to headquarters for the remainder of analyses.

Acidity was determined according to the Salotto[6] method of adding hydrogen peroxide and titrating potentiometrically to a pH 7.3 end point. Total iron, calcium, magnesium, manganese, and aluminum concentrations were determined by atomic absorption spectrophotometry.[7] EPA Methods[7] was used for the sulfate determination. The pH was measured potentiometrically. Ferrous iron was determined by colorimetrically titrating potassium dichromate against a p-Diphenylamine sulfonic acid sodium salt indicator.[8] A YSI Model 51 dissolved oxygen meter was used for dissolved oxygen measurements.

The Rex Chainbelt laboratory, in addition to the above determinations, analyzed for silica by atomic absorption. A Hach kit was used by Rex Chainbelt for on-site determinations of calcium, total hardness, total iron, ferrous iron, and sulfates. A Myron L TDS meter was used for TDS measurements.

Physical Measurements and Calculations

All flows were measured volumetrically except for spiral wound recycle brine flow for which a rotameter was used. Since product flow was strongly dependent upon temperature, careful temperature measurements were made. Recovery was defined as product flow ÷ feed flow x 100 where feed flow equalled brine flow plus product flow.



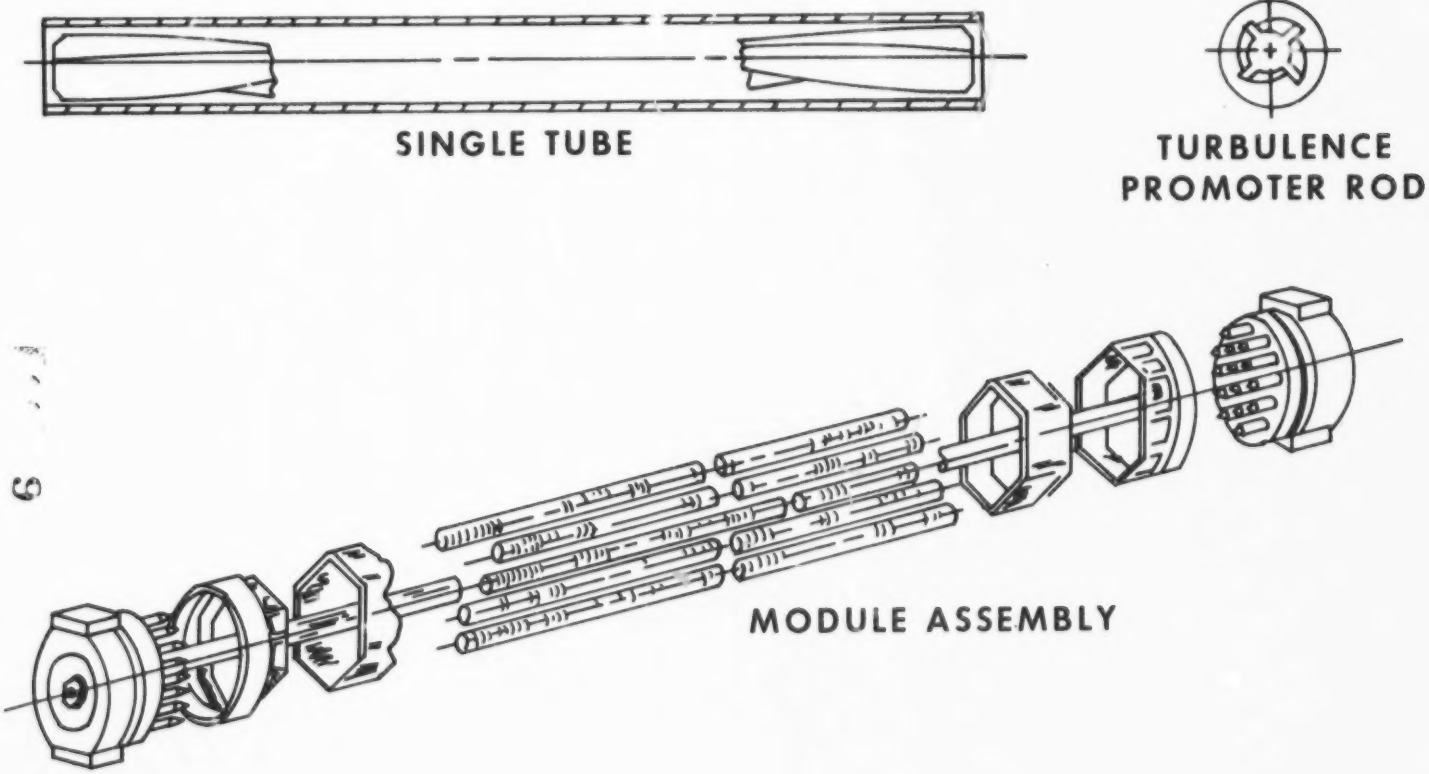


FIGURE 5

TUBULAR RO MODULE CONFIGURATION

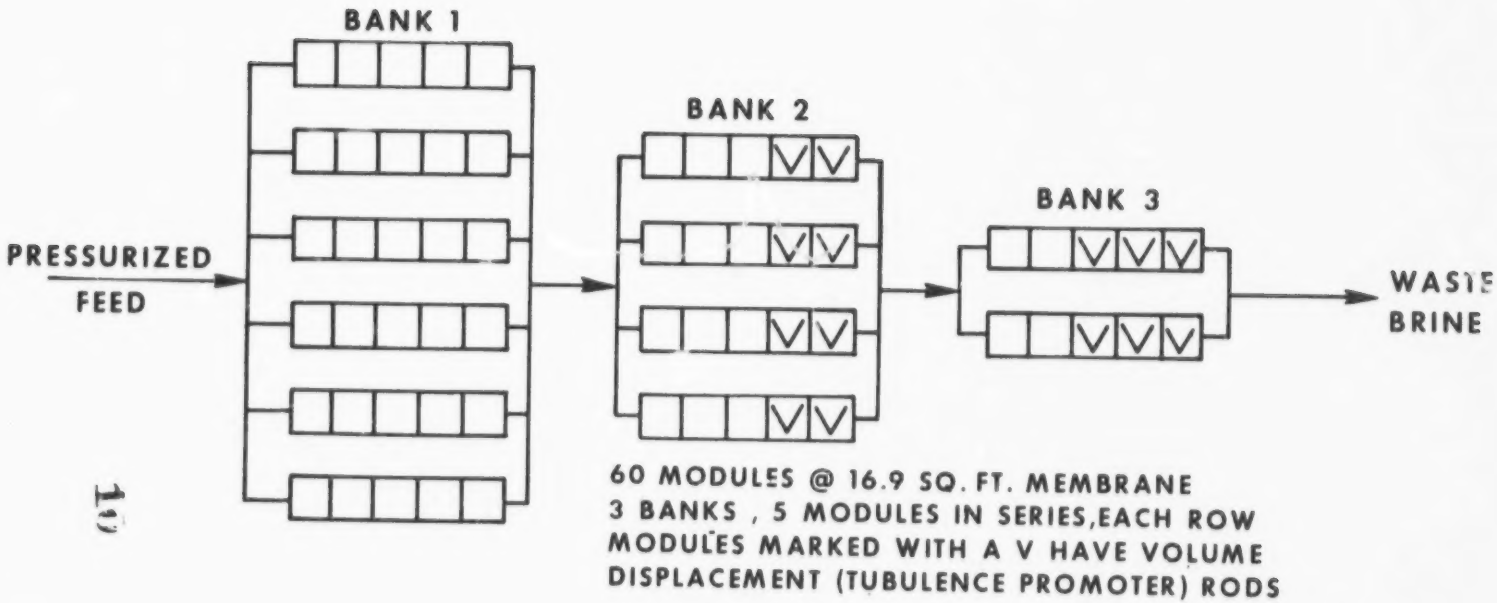


FIGURE 6

INITIAL MODULE ARRANGEMENT TUBULAR RO SYSTEM

The standard way of expressing membrane performance is in gallons of product flow per square foot of membrane per day at a specified temperature and net pressure. To obtain these values, product flow was corrected from the observed temperature to 77° F by a correction chart supplied by each manufacturer. In general, product flow increased roughly 1.5 - 2 percent per degree Fahrenheit.

Average pressure was determined by reading gauge pressures in and out of each vessel and averaging them. Osmotic pressure, which in this study was mathematically correlated to conductivity, was subtracted from the average applied pressure to give net driving pressure.

Therefore flux rates were determined according to the following equation:

Flux (gal/ft^2/day @ 77° F & Desired Net Pressure) = Product Flow (gpm) at observed temperature * correction factor to 77° F ÷ (Average pressure -Osmotic pressure) psi net ÷ membrane area (ft^2) x 1440 minutes/day x Desired Net Pressure.

Salt rejection measures the ability of a membrane to reject specific ions, therefore rejection is a measure of the efficiency of a membrane in separating pollutants from the product water by being relatively impermeable to the passage of salts.

This measurement is generally made in reference to concentrations in the water quality entering the reverse osmosis unit as compared to system product quality. For this paper, salt rejection equalled (Conc. Influent - Conc. Product) x 100/Conc. Influent. In the cases of the hollow fiber and tubular units, the influent was raw acid mine drainage. For the spiral wound, blended feed was the influent to the unit.

Membrane performance, deterioration, and fouling were evaluated by plotting flux values on log-log paper and calculating log-log flux decline slopes from the line of best fit.

Taking values from the graph, the slope was calculated by the following equation:

$$\text{Slope} = \frac{\text{Log Flux}_2 - \text{Log Flux}_1}{\text{Log Time}_2 - \text{Log Time}_1}$$

Since flux rates generally decrease with time, these flux decline slopes are negative, indicative of the downward trend. Flux decline slopes less than -0.05 indicate very little fouling occurring.

RESULTS

As a prelude to actual field investigations, laboratory studies were performed by Rex Chainbelt to attempt to isolate possible causes for the severe iron fouling seen at Mocanaqua during their 1969 tests. From the results of these batch tests, Mason postulated that the most probable cause of the observed fouling was bacterial oxidation of ferrous iron at the membrane surface and subsequent precipitation of the resulting ferric iron which had been hydrolyzed.

For this reason, ultraviolet (UV) disinfection lights were installed as part of the pretreatment system for all three units tested in the field. It was felt that the UV light would kill most of the iron oxidizing bacteria and thus inhibit or prevent bacterial oxidation of Fe^2 to Fe^3.

A series of iron oxidation studies were performed during the actual field study to evaluate the effectiveness of the UV light. Figure 7 presents one set of data collected on the iron oxidation rates of four different samples. The four samples were stored in polyethylene bottles. Once each day the cap was removed and then replaced to allow oxygen equalization. The sample was then shaken vigorously to insure an oxygen saturated sample. The raw AMD filtered through a 10 micron filter exhibited a rapid and immediate reduction in iron (II) level. On the other hand a filtered sample in which the pH was adjusted to 2.5 experienced little iron (II) oxidation for a period of 100 hours and then a rapid reduction at approximately the same rate as the sample which had no pH adjustment. The sample which had been exposed to ultraviolet radiation had little decrease in iron II level until 100 hours and then a gradual decrease until no iron (II) remained at 350 hours. The sample disinfected with formaldehyde had little decrease in iron (II) level when the experiment ended at 676 hours (iron II was 42 mg/l at this time).

Additional studies compared the effects of daylight, darkness, and ambient temperature on the oxidation rates and concluded that daylight inhibited the oxidation rate and that the rate of oxidation increased with temperature.

At the completion of these oxidation studies it was apparent that iron oxidizing bacteria were responsible for the rapid decrease in iron (II) levels since the oxidation rate exceeded the chemical oxidation rate by many orders of magnitude.[10] It was also apparent that the oxidation was inhibited by lowering the pH to 2.5. This result is not surprising, since changes in pH can upset biological mechanisms until the organisms acclimate to the new pH level. In addition, lowering the pH served to inhibit ferric precipitation even if the ferrous iron did oxidize. These studies confirmed that UV disinfection was a satisfactory choice for pretreatment.

It was necessary to determine the osmotic pressure of the water in order to compensate for variations in water quality and recovery. The spiral wound unit was modified[11] to enable measurement of osmotic pressure by pressure differences between the brine and product side of the membrane. By varying recovery, osmotic pressure measurements were made over a complete range of concentrations and a correlation was developed between brine conductivity and osmotic pressure. Since acid injection was utilized in Phase II spiral wound studies and acid affects conductivity, a different correlation was necessary for Phase II. Both equations and plots are shown in Figure 8.

Spiral Wound Phase I Studies

Phase I of the spiral wound studies was made at a unit recovery of 75 percent and system operating pressure of 600 psi. A summary of operating parameters for this study is given in Table 2. Overall system recovery during Phase I was maintained at 75 percent during the first 1054 hours of operation. The log-log flux decline slope was -0.034 for tube one and -0.032 for tube three during this period. At 1054 hours elapsed time, the ultraviolet light was turned off to determine its effectiveness in controlling flux decline. As shown in Figure 9 (linear plot) and Figure 10 (log-log plot), the increase in flux decline was dramatic with the log-log slope increasing to near -0.2 even

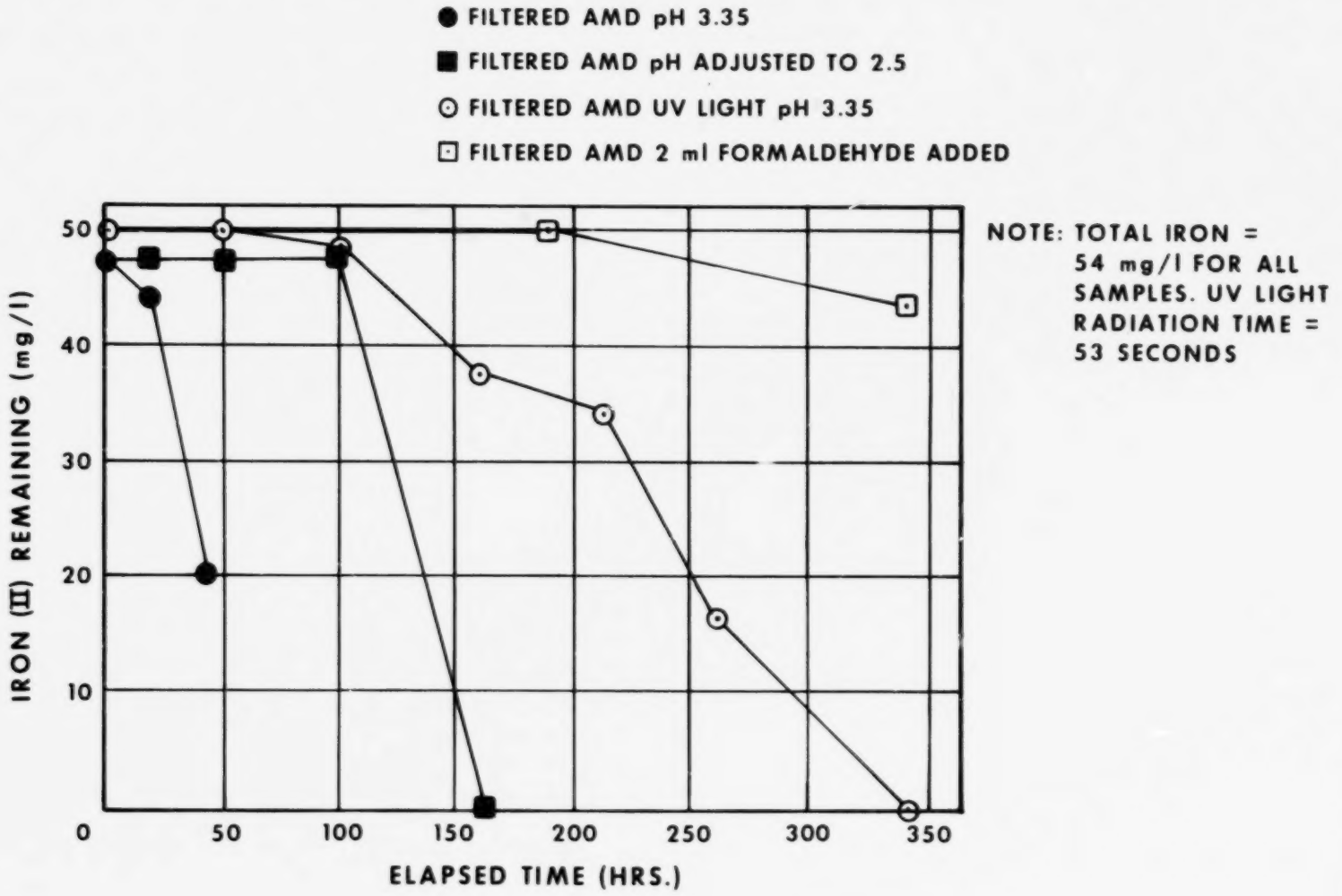


FIGURE 7
IRON OXIDATION RATES

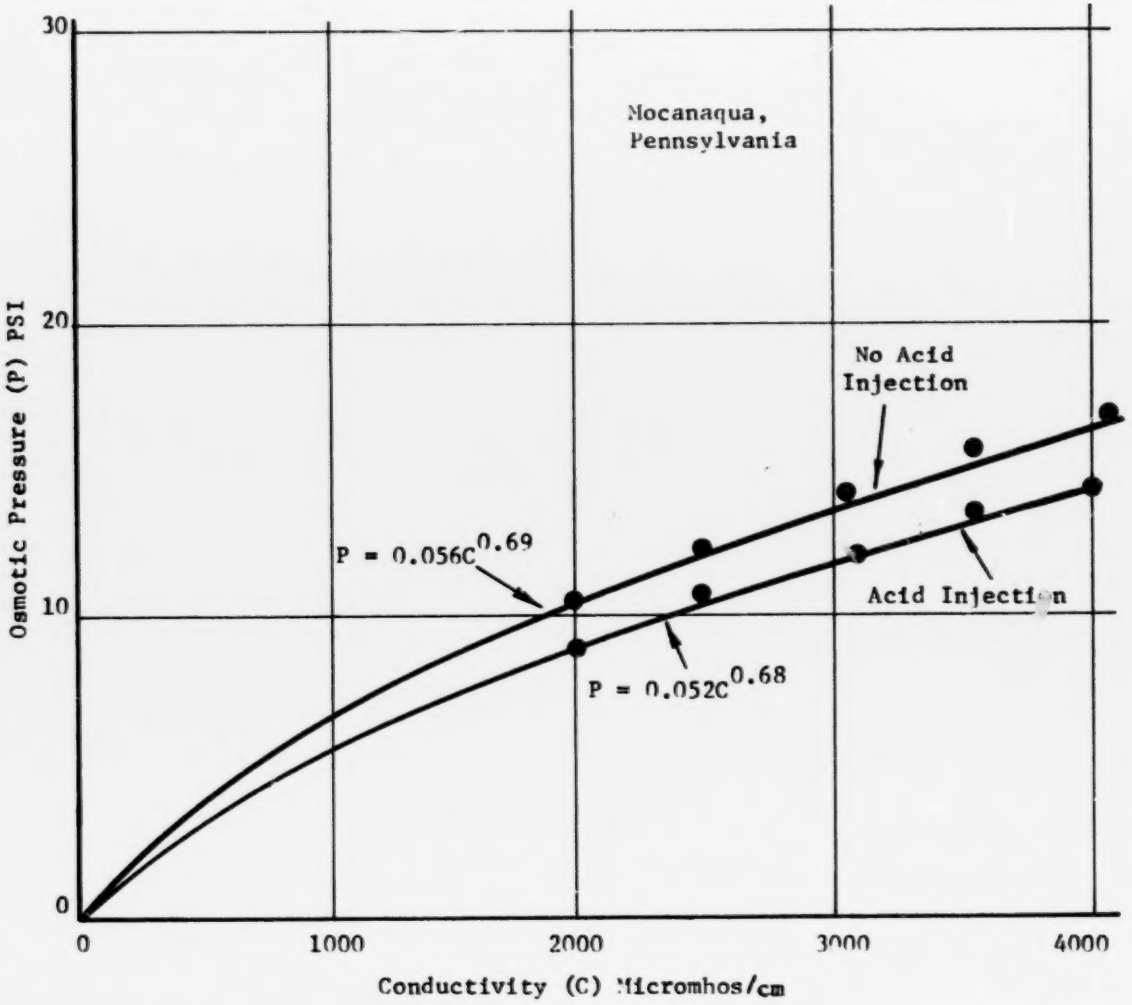


FIGURE 8
OSMOTIC PRESSURE - CONDUCTIVITY RELATIONSHIPS

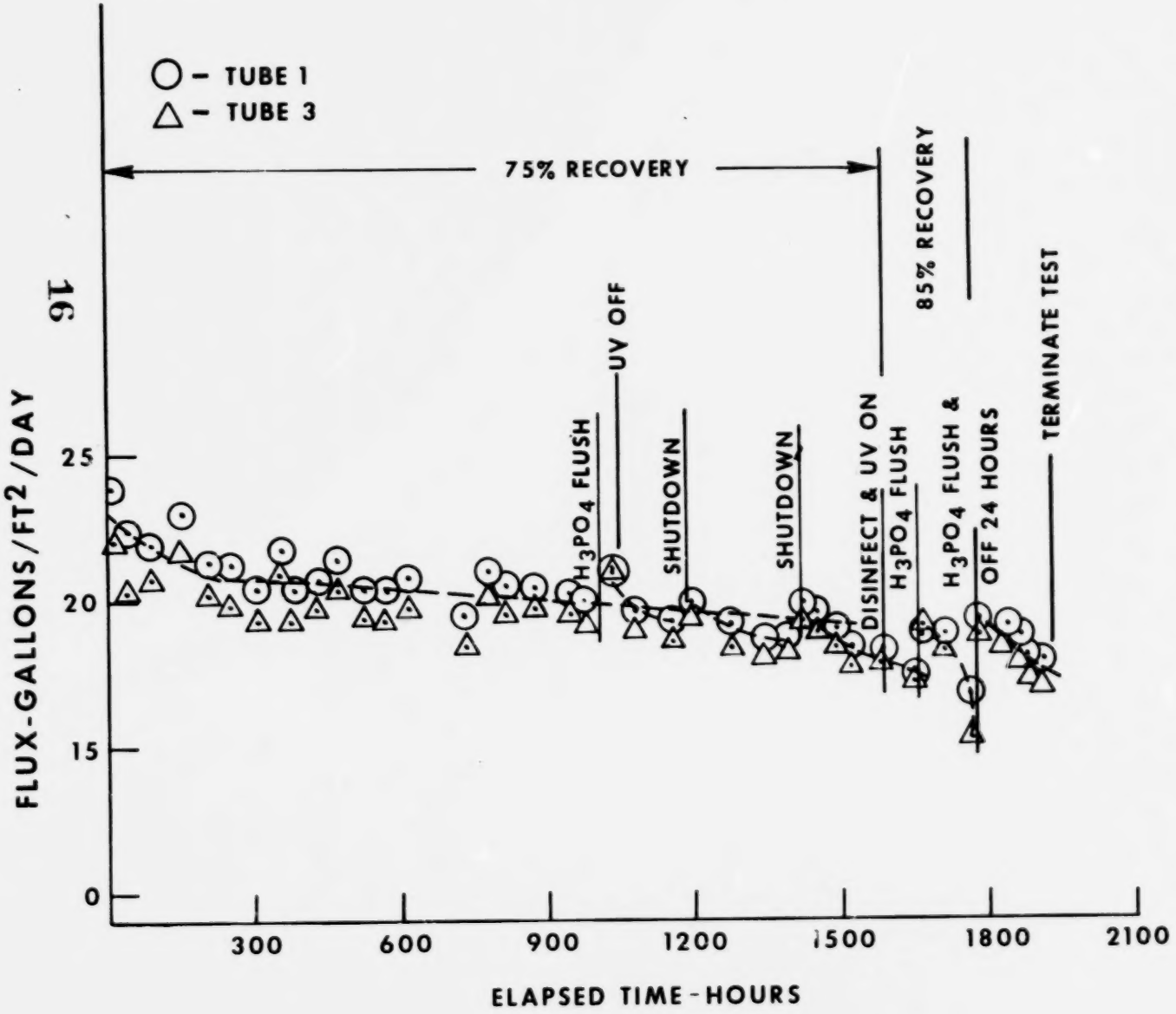
Table 2
Operating Parameters*
Spiral Wound Phase I Study @ 75 Percent Recovery

Raw Water Feed Flow	gpm	6.02
Product Water Flow	gpm	4.50
Brine Water Discharged	gpm	1.52
Brine Water, Recycled	gpm	4.26
Minimum Brine/Product Flow Ratio (Tubes 1 and 2)	ratio/module	5:1
Maximum Brine/Product Flow Ratio (Tube 3)	ratio/module	12:1
Water Recovery	Percent	74.8
Recovery of Blended Feed	Percent	43.8
Feed Pressure	psig	602
Feed Water Temperature	°F	62.6
Tube One Flux, gal/ft^2/day @ 600 psi Net and 77° F		19.56
Tube Two Flux, " " "		19.52
Tube Three Flux " " "		18.77
Length of Run	Hours	1672
Date of Run		May 1 - July 12, 1971

*All values are means from 73 data sets.

FIGURE 9

SPIRAL WOUND 4,000 GPD R.O. UNIT FLUX RATES-PHASE I



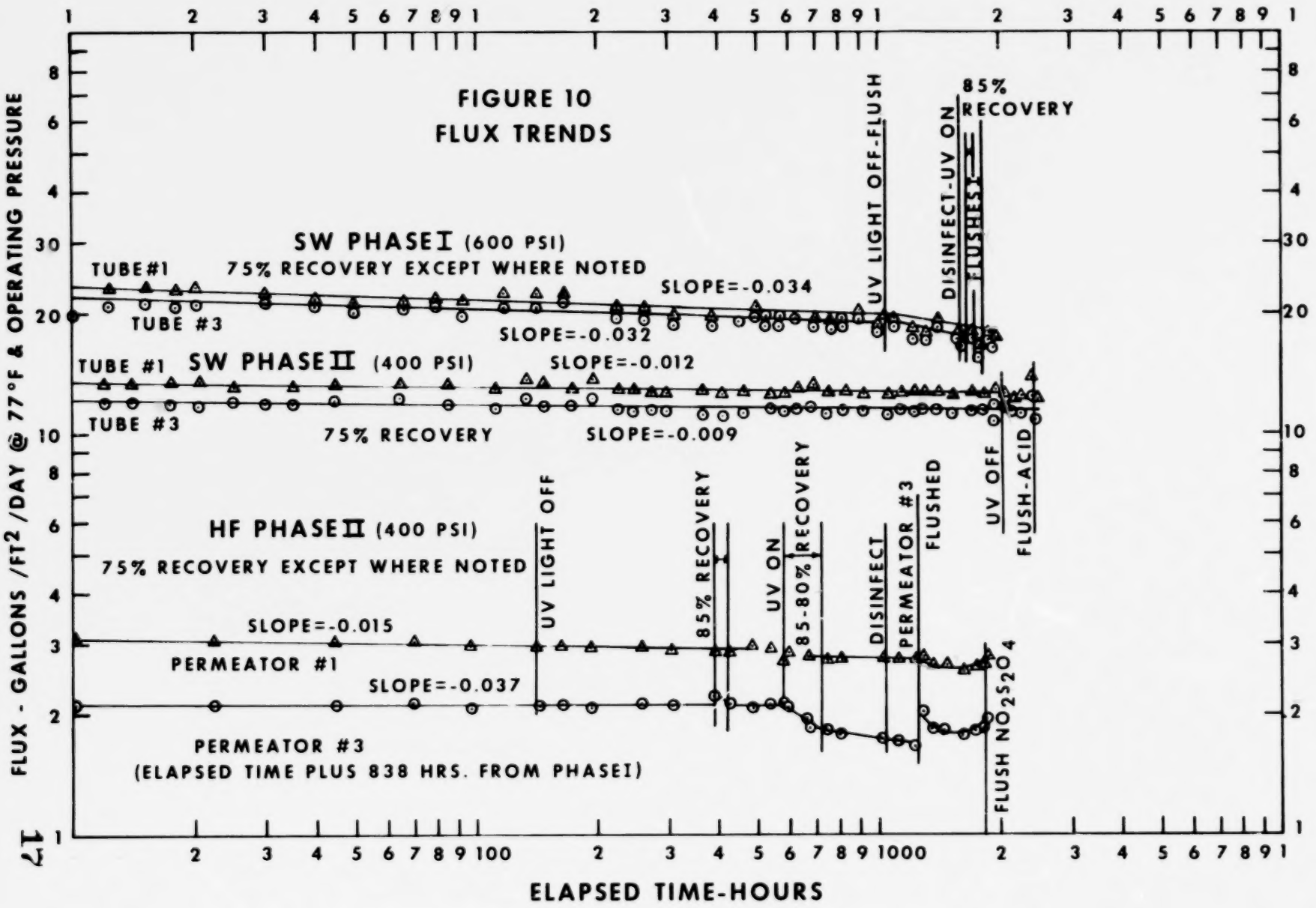


FIGURE 10
FLUX TRENDS
SW PHASE I (600 PSI)
TUBE #1
75% RECOVERY EXCEPT WHERE NOTED
SLOPE=-0.034
TUBE #3
SLOPE=-0.032
UV LIGHT OFF-FLUSH
DISINFECT-UV ON
FLUSHED
85% RECOVERY
TUBE #1
SW PHASE II (400 PSI)
SLOPE=-0.012
TUBE #3
75% RECOVERY
SLOPE=-0.009
UV OFF
FLUSH-ACID
HF PHASE II (400 PSI)
75% RECOVERY EXCEPT WHERE NOTED
UV LIGHT OFF
85% RECOVERY
UV ON
85-80% RECOVERY
DISINFECT
PERMEATOR #3
FLUSHED
SLOPE=-0.015
PERMEATOR #1
SLOPE=-0.037
PERMEATOR #3
(ELAPSED TIME PLUS 838 HRS. FROM PHASE I)
FLUSH $NO_2S_2O_4$
FLUX - GALLONS /FT^2 /DAY @ 77°F & OPERATING PRESSURE
ELAPSED TIME-HOURS

though recovery remained at 75 percent. Following a phosphoric acid flush, the UV was turned on again but recovery was increased to 84 percent. Flux decline was so severe at 84 percent recovery (log-log slope greater than -4.0) that the run was terminated after only 70 hours at that recovery level and flushed again with phosphoric acid. Though the acid flush improved flux, it did not stabilize on the original slope, presumably indicating all the fouling had not been removed. Total operating time during Phase I was 1922 hours.

Fouling observed at 84 percent recovery was attributed to calcium sulfate precipitation. However, at 75 percent recovery and the UV off, it was felt that bacterial propogated iron precipitation was causing the flux decline. Analysis of the acid flush water confirmed the presence of large amounts of both iron and calcium after the 84 percent recovery run.

Operating parameters for the spiral wound unit during the 84 percent recovery run are given in Table 3.

Chemical analyses for the 75 percent recovery operation are presented in Table 4 and indicate a 99+ percent rejection of all multivalent ions. Product waters would still require treatment for iron and manganese and pH adjustment before potable water quality criteria could be met.

Spiral Wound Phase II

The manufacturer suggested that increasing the brine/product (b/p) flow ratio would decrease the log-log slope observed during Phase I. One way of accomplishing a b/p increase was to lower the operating pressure and thereby reduce product flow. Lowering input pressure to 400 psi would also serve to lessen membrane compaction which contributes to flux losses. During Phase I, the maximum brine/product ratio per module was 12:1, the minimum was 5:1 (from Table 2). During Phase II, the maximum b/p ratio was 22:1 and the minimum 10:1 (Table 5) which amounted to about a 200 percent increase over Phase I.

As the earlier oxidation tests had shown pH control to be an effective oxidation inhibitor and as the lower pH would also inhibit precipitation of the ferric iron already present, sulfuric acid was injected into the feed water to lower the blended feed pH to 2.9. The ultraviolet light was also used during the majority of this Phase II study.

Table 5 presents the operating parameters for this 2454 hour Phase II study at 75 percent recovery.

Early in the study, leaks were observed in tubes one and two. By probing each module and measuring the conductivity of product water at various points along the inside of the modules' product tubes, it was determined that all leaks were located near the ends of the modules where glue connected membrane to the perforated product tube (see Figure 1). It was decided not to replace the modules since considerable operating time would be lost and since modules in tube three had no leaks, their product quality would be representative of normal modules. Also, as the leaks in tube one and two were very small, they would have no effect on flux studies. Therefore, chemistry data in Table 4 is given for product water from tubes 1 and 3 as well as for the entire unit.

Table 3

Operating Parameters - Spiral Wound Phase I Study
@ 84 Percent Recovery

Raw Water Feed Flow	gpm	4.92
Product Water Flow	"	4.13
Brine Water Discharged	"	0.79
Brine Water Recycled	"	5.50
Minimum Brine/Product Flow Ratio (Tubes 1 & 2)	ratio/module	8:1
Maximum Brine/Product Flow Ratio (Tube 3)	ratio/module	12:1
Water Recovery	Percent	83.9
Recovery of Blended Feed	"	39.6
Feed Pressure	psig	600.0
Feed Water Temperature	°F	66.6
Tube One Flux, gal/ft^2/day @ 600 psi net and 77° F		17.03
Tube Two Flux, gal/ft^2/day @ 600 psi net and 77° F		17.06
Tube Three Flux, gal/ft^2/day @ 600 psi net and 77° F		16.25
Length of Run	Hours	70
Date of Run		July 13 - July 17, 1971

All values are means from four data sets

Table 4
Chemical Analyses - Spiral Wound Studies
Analyses by EPA

Sample Designation	pH	Cond.	Acidity	Calcium	Magnesium	Total Iron	Ferrous Iron	Aluminum	Sulfate	Manganese	Dissolved Oxygen
Spiral Wound Phase I @ 75 Percent Recovery											
Raw Feed	3.4	1080	240	130	88	77	64	12	750	-	< 1.0
Blended Feed	3.1	2070	460	260	170	180	130	24	1340	-	< 1.0
Brine	2.9	3540	810	490	310	330	250	44	2300	-	< 1.0
Product	4.4	17	38	0.4	0.3	0.4	0.3	0.2	0.9		
Rejections*		99.2%	91.7%	99.8%	99.8%	99.8%	99.8%	99.2%	99.9%		
Spiral Wound Phase II @ 75 Percent Recovery											
Raw Feed	3.4	1110	220	140	110	100	73	14	930	17	
Acidified Feed	2.9	1520	420	140	110	100	77	14	980	17	
Blended Feed	2.8	2830	610	330	260	250	190	33	2110	43	
Brine	2.7	4150	880	520	380	370	280	54	3130	68	
Total Product	3.8	67	33	1.3	4.0	2.4	2.0	0.8	19	0.5	
Overal Rejections*		97.6%	94.6%	99.6%	98.5%	99.0%	98.9%	97.6%	99.1%	98.8%	
Tube 1		86	-	1.6	3.1	3.3	-	1.1	30	0.6	
Rejections*		97.0%		99.5%	98.8%	98.7%	-	96.7%	98.6%	98.6%	
Tube 3		37		0.55	0.75	0.68	-	0.75	5.8	0.21	
Rejections*		98.7%		99.8%	99.7%	99.7%		97.7%	99.7%	99.5%	

*Rejections = Blended Feed - Product/Blended Feed x 100

Note: All units are mg/l except pH and Specific Conductance (Micromhos/cm)

Table 5
Operating Parameters*
Spiral Wound Phase II Study @ 75 Percent Recovery

Raw Water Feed Flow	gpm	5.18
Product Water Flow	"	3.86
Brine Water Discharged	"	1.32
Brine Water Recycled	"	6.32
Minimum Brine/Product Flow Ratio (Tubes 1 & 2)	ratio/module	10:1
Maximum Brine/Product Flow Ratio (Tube 3)	"	22:1
Water Recovery	percent	74.5
Recovery of Blended Feed	"	33.6
Feed Pressure	psig	399
Feed Water Temperature	°F	66.6
Tube One Flux, gal/ft^2/day @ 400 psi Net and 77° F		12.81
Tube Two Flux, gal/ft^2/day @ 400 psi Net and 77° F		12.55
Tube Three Flux, gal/ft^2/day @ 400 psi Net and 77° F		11.58
Length of Run	hours	2,454
Date of Run		July 27 - November 9, 1971

*All values are means from 100 data sets

Although unit rejections were lower for Phase II than for Phase I due to the leaks, tube 3 rejections were comparable to Phase I results.

A log-log plot of Phase II flux is given in Figure 10. Log-log slopes of -0.012 for tube 1 and -0.009 for tube 3 were obtained during the 2454 hours of operation at 75 percent recovery. These values were improvements over the -0.034 slopes from Phase I. It is felt that the combination of acid injection to inhibit precipitation of ferric hydroxide and the higher brine/product ratios and brine flow rates were definitely responsible for the flux stabilization. Discontinuing use of the ultraviolet light at 2002.5 hours elapsed time had no apparent effect on flux stability.

It is possible that the higher brine/product ratio and correspondingly higher brine flow rates--or acid injection alone--may have been solely responsible for flux improvement but unfortunately, no tests were made to prove or disprove this conjecture.

A phosphoric acid flush at the termination of the 2454 hour study did not improve flux.

Approximately 60 mls of sulfuric acid (98 percent - technical grade) were required to treat each 1000 gallons of water entering the reverse osmosis unit in order to lower blended feed pH to 2.9. This amounted to 27 mg of concentrated acid per liter of water treated.

Hollow Fiber

Phase I hollow fiber testing began with a single permeator operating at 75 percent recovery at 400 psi and continued for a total of 838 hours. Operating parameters are given in Table 6 and chemical data is presented in Table 9.

Rejections of all multivalent ions were in the range of 99 percent based on raw feed. These rejections, though slightly less than the spiral wound, were still excellent. As in the case of the spiral wound, product water would require treatment for pH, iron, and manganese before potable standards could be met.

The flux trend for the single hollow fiber permeator is shown linearly in Figure 11 and on a log-log basis in Figure 12. The log-log flux decline slope was -0.037 during the 838 hour study. This flux decline slope was comparable to Phase I spiral wound results. A small increase in pressure drop across the permeator was observed which probably indicated minor iron fouling.

Phase II Hollow Fiber

For Phase II studies, two additional permeators were added to the Phase I system to form a 2-1 array as shown in Figure 4. The Phase I permeator which had accumulated 838 hours of operation was used as the last permeator in the array. The permentors were operated in this 2-1 array to allow high recovery experiments and confine the expected calcium sulfate fouling to a single permeator. Generally, hollow fiber units are not used in staged arrays but are arrayed for parallel operation since brine flow requirements for hollow fiber systems are not as critical as for tubular and spiral wound systems.

During Phase II, several variations in operating parameters were made. In order to evaluate the effect of the ultraviolet light on system operation,

Table 6
Operating Parameters*
Hollow Fiber Phase I Study @ 75 Percent Recovery

Raw Water Feed Flow	gpm	2.08
Product Water Flow	"	1.55
Brine Water Discharged	"	0.53
Water Recovery	percent	74.4
Feed Pressure	psig	400.0
Feed Water Temperature	°F	53.3
Unit Flux, gal/ft^2/day @ 77° F & 400 psi Net		2.32
Length of Run	hours	838

*All values are means from 78 data sets

the light was turned off from 140 hours elapsed time through 595 hours e.t. This time interval represented 978-1433 hours e.t. on permeator number 3 (last stage permeator). As seen in Figure 10, no apparent flux trend change occurred as a result of no UV. This was opposite to the dramatic slope change which occurred on spiral wound when the UV was turned off.

At 390 hours through 426 hours e.t., the system recovery was increased to 85 percent. This increase in system recovery had very little effect on the recoveries of permeators one and two whose recoveries were still below 65 percent. Thus, very little change in flux occurred in the first two permeators during this high system recovery operation. However, permeator three which was subject to the most severe pollutant concentrations, suffered a drastic flux loss. Upon lowering recovery again to 75 percent, permeator three's flux again stabilized (Figure 11).

At 596 hours elapsed time (1433 for permeator three) the ultraviolet light was turned on again but system recovery was increased to 85 percent. These operating conditions were maintained for 111 hours, including operating at 80 percent recovery for 38 hours, before system recovery was lowered (707 hours e.t., 1545 e.t. for permeator number three).

Again, severe flux losses occurred in permeator three (log-log slope = 1.7). Although permeator three's flux stabilized, it was now following a significantly steeper flux decline slope (log-log slope = -0.36 at 78-80 percent recovery). A subsequent flush with disinfectant failed to improve flux. Sodium hydrosulfide was used to flush permeator three at 2081 hours (on number three) and successfully restored flux to the original flux decline slope of -0.037 at 78 percent recovery. However, flux immediately dropped again but stabilized at lower values until the end of the run at 2670 hours e.t. (number three permeator).

Permeators one and two appeared to suffer a flux slope change near 600 hours elapsed time after following an initial slope of -0.015 until that time. Following the 85 percent recovery test which ended at 707 hours elapsed time, first stage permeator flux stabilized following a log-log slope of -0.03 for approximately 540 hours until 1243 hours e.t. During the last 590 hours of operation, all three permeators lost and then regained flux prior to a final sodium hydrosulfide flush. The flush virtually restored first stage permeator flux to the original -0.015 slope values. Since the test was terminated at this point, it was not possible to determine if the -0.015 slope could be maintained following the flush. Although the flush improved permeator three's flux, it did not return it to the original slope values.

A post mortem analysis of permeator number three by the manufacturer revealed that the fouling was largely due, as expected, to calcium sulfate precipitation.

In the case of the two first stage permeators whose flux had been restored by the final flush, an additional 31 psi pressure drop had been acquired during the study which was not removed. Since neither of these first stage permeators had ever operated above 66 percent recovery, it must be assumed that iron fouling caused the flux losses and pressure drop increase.

Operating parameters for Phase II hollow fiber at 75 and 85 percent recovery are given in Tables 7 and 8 respectively. Chemical data from 75 percent recovery is reported in Table 9.

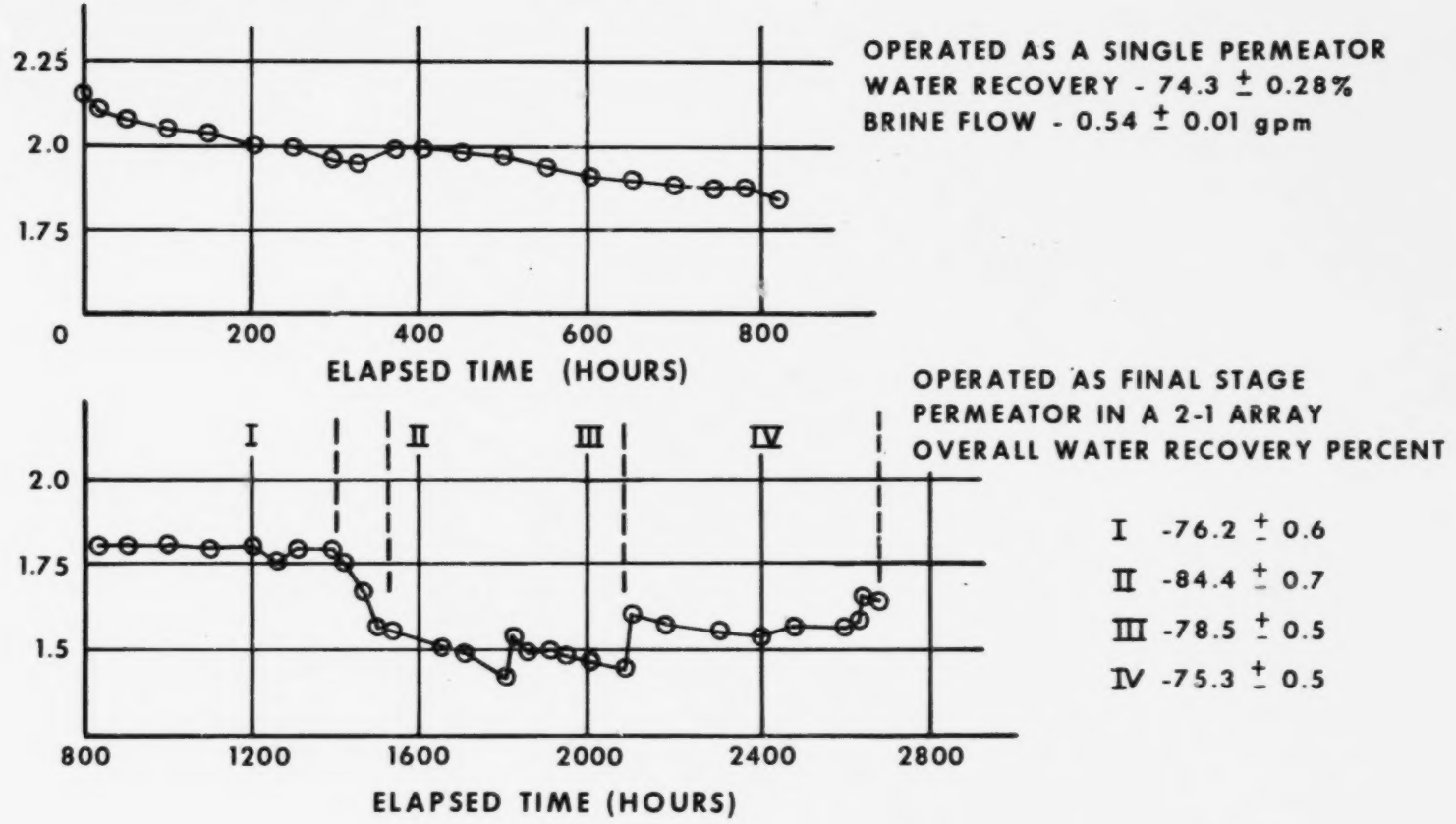


FIGURE 11

HOLLOW FIBER RO OPERATION PERMEATOR #691

Table 7
Operating Parameters*
Hollow Fiber Phase II Study @ 75 Percent Recovery

Raw Water Feed Flow	gpm	6.18
Total Product Flow	"	4.72
Brine Water Discharged	"	1.46
Unit Water Recovery	percent	76.4%
Feed Pressure	psig	400
Feed Temperature	°F	54.3
Permeator No. One Product Flow	gpm	1.86
Recovery, Permeator No. One	percent	59.9
Flux, Permeator No. One, gal/ft^2/day @ 400 psi Net & 77° F		2.78
Permeator No. Two Product Flow	gpm	1.83
Recovery, Permeator No. Two	percent	59.5
Flux, Permeator No. Two, gal/ft^2/day @ 400 psi & 77° Net		2.74
Permeator No. Three Product Flow	gpm	1.03
Recovery, Permeator No. Three	percent	41.4
Flux, Permeator No. Three, gal/ft^2/day @ 400 psi Net & 77° F		1.92
Length of Run	hours	1667
Date of Run		June 10 - August 28, 1971

*All values are means from 83 data sets

Table 8
Operating Parameters*
Hollow Fiber Phase II Study @ 85 Percent Recovery

Raw Water Feed Flow	gpm	5.73
Total Product Flow	"	4.86
Brine Water Discharged	"	0.87
Unit Water Recovery	percent	84.8
Feed Pressure	psig	400
Feed Temperature	°F	54.0
Permeator No. One Product Flow	gpm	1.89
Recovery, Permeator No. One	percent	65.5
Flux, Permeator No. One, gal/ft^2/day @ 400 psi Net & 77° F		2.84
Permeator No. Two Product Flow	gpm	1.85
Recovery, Permeator No. Two	percent	65.0
Flux, Permeator No. Two, gal/ft^2/day @ 400 psi Net & 77° F		2.78
Permeator No. Three Product Flow	gpm	1.12
Recovery, Permeator No. Three	percent	56.3
Flux, Permeator No. Three, gal/ft^2/day @ 400 psi Net & 77° F		2.10
Total Operating Time @ 85 Percent Recovery, hours		147
Longest Run	hours	111
Date of Run	6/26-6/28/71,	7/5 -7/9/71

*All values are means for 11 data sets

Rejections during Phase II were comparable to Phase I results, i.e. in the range of 99 percent based on raw feed.

A complete log-log flux plot for the initial permeator which was used both in Phase I and Phase II is given in Figure 12. A total operating time of 2670 hours was acquired by this permeator (838 during Phase I and 1832 during Phase II).

Significant variations were noted in the log-log flux curve of the hollow fiber unit. The slope appeared to increase as brine flow decreased and a possible relationship may exist in the form of a brine/product flow limit although insufficient data was available to substantiate this relationship. As brine flow rates decreased, recovery and risk of precipitation increased and this may have caused the observed slope changes. Whatever the reason, flux slopes were minimized when the brine flow rate was in excess of one gallon per minute.

Tubular Unit

The tubular reverse osmosis system was also operated in two separate phases during this study. Phase I utilized 60 Type 310 modules in a 6-4-2 array with 5 modules in series in each row. The last two modules in bank 2 and the last 3 modules in bank 3 contained volume displacement rods (VDR) which increased the brine velocity. The normal inside diameter in the tubular system is one-half inch which corresponds to a linear brine velocity of 1.64 fps per gpm of brine flow. The volume displacement rods effectively increased this velocity to 2.5 fps per gpm of brine flow. When utilizing VDR's the headloss through the module increased significantly. In a module without the VDR's the headloss at one gpm brine flow was five psi per module, while with VDR's this increased to 22 psi per module.

Initial Phase I operation was at 600 psi and 75 percent recovery. During Phase I the product water flux decreased steadily from 13 gsfd to 8.5 gsfd in only 480 hours. It was originally assumed that the system had been contaminated with iron oxidizing bacteria because of trouble experienced with the UV light. At 160 hours the system was disinfected with a quatenary ammonium compound (L-11-X) and a slight increase in flux was noted, since the membranes were relaxed (operated at low pressure) and this generally results in a flux increase for a short period of time. Immediately after the disinfection, the flux continued to decline rapidly. At this point, it was felt that the brine velocities might possibly be too low and that concentration polarization effects were the cause of the rapid fouling. It was therefore decided to increase the brine velocities. The minimum brine velocity was increased from 1.2 - 1.4 feet per second to 2.0 - 2.2 fps.

Phase I chemical data is presented in Table 11.

At the end of Phase I it was noted that the flux declines experienced with the tubular system were not experienced with the hollow fine fiber system or the spiral wound system also operating alongside. It was also noted that both the spiral wound system and the hollow fiber system had considerably lower salt passage (higher rejection) as compared to the tubular system. The high salt passage of the tubular 310 membrane may have had some influence on the flux declines experienced. To test this, five high flux-low salt passage modules (type E610) were installed and put into operation for Phase II. During Phase II, recovery was limited to less than 50 percent at 600 psi due to the use of only five modules. Operating parameters for this 807 hour study

are given in Table 10 and chemical data is presented in Table 11. Rejections were higher for Phase II (type 610) membranes than for Phase I membranes (type 310). Figure 12 presents the flux history for these modules. An extremely high initial compaction set was experienced during the first few hours of operation. The flux then stabilized on a -0.040 log-log slope for the first 300 hours. A gradual decline then occurred through about 440 hours, at which time the flux stabilized at 13.7 gsfd for the remainder of the study. The flux decline slope change experienced from near 300 hours e.t. was also noticed to a lesser degree on the hollow fiber unit and was believed caused by a higher than normal iron (III) content in the AMD. The decline was probably entirely due to iron fouling, since operation at 40-45 percent recovery was well below the $CaSO_4$ fouling range. The modules were flushed with a sodium-hydro-sulfite solution (4 wt percent) for one hour. This resulted in a dramatic increase in flux as shown in Figure 12. Since additional operating time was not available, it is not known how much of this flux increase was due to cleaning and how much was due to membrane relaxation. It is felt, however, that a substantial gain was accomplished, since membrane relaxation alone would not account for an increase in flux of about 33 percent.

The salt passage properties for both the types 310 and 610 tubular modules are shown in Table 12. The salt passage was calculated based on average brine concentration experienced on the membrane, i.e. the average of feed and brine concentrations. This procedure allows comparison of salt passage while operating the R.O. system at different product water recoveries.

Generally salt passage for the type 310 modules was in the range of 1 to 1.5 percent for Ca, Mn, Fe, Al, and SO_4. Silica passage was extremely high at an average percent of 54. The type 610 modules had significantly lower salt passage in the range of 0.4 to 0.5 percent for Ca, Mg, Mn, Fe, Al, and SO_4. Silica passage was also considerably lower than the 310 modules at an average percent of 6.2 percent passage. No apparent changes occurred in the salt passage throughout the operational period.

The mechanical operation of the tubular system was excellent. No module failures were experienced over the entire 2800 hour operation. This reflects the improvements made in tube construction since the last study.[1]

In summary a number of points can be made regarding tubular system operation. The use of volume displacement rods is definitely not recommended. The price paid in headloss far exceeds the benefits obtained. If higher velocities are required, it appears recirculation of brine would be the preferred alternative. With regard to required velocities, it appears that a minimum velocity of about 1.5 fps is desirable, since operation at this velocity with the higher flux-low salt passage modules was satisfactory. It should be noted, however, that the recoveries during Phase II were quite low (45-70 percent), and that operation at higher recoveries may require higher velocities to offset the concentration polarization effects due to higher brine concentrations. Additional study at higher recoveries is necessary to answer this question.

It is not known if the high initial flux loss experienced during Phase I with the type 310 modules was specific for the modules utilized or a result of the higher salt passage. In any event, low salt passage modules are definitely recommended for both flux and product water quality considerations.

Table 10
Operating Parameters*
Tubular Phase II Study @ 43 Percent Recovery

Raw Water Feed Flow	gpm	1.48
Product Water Flow	"	0.63
Brine Water Discharged	"	0.85
Water Recovery	percent	42.5
Feed Pressure	psig	617.0
Feed Water Temperature	°F	55.0
Unit Flux, gal/ft^2/day @ 77° F & 600 psi Net		15.60
Length of Run	hours	807

*All values are means from 34 data sets

FIGURE 12
FLUX TRENDS

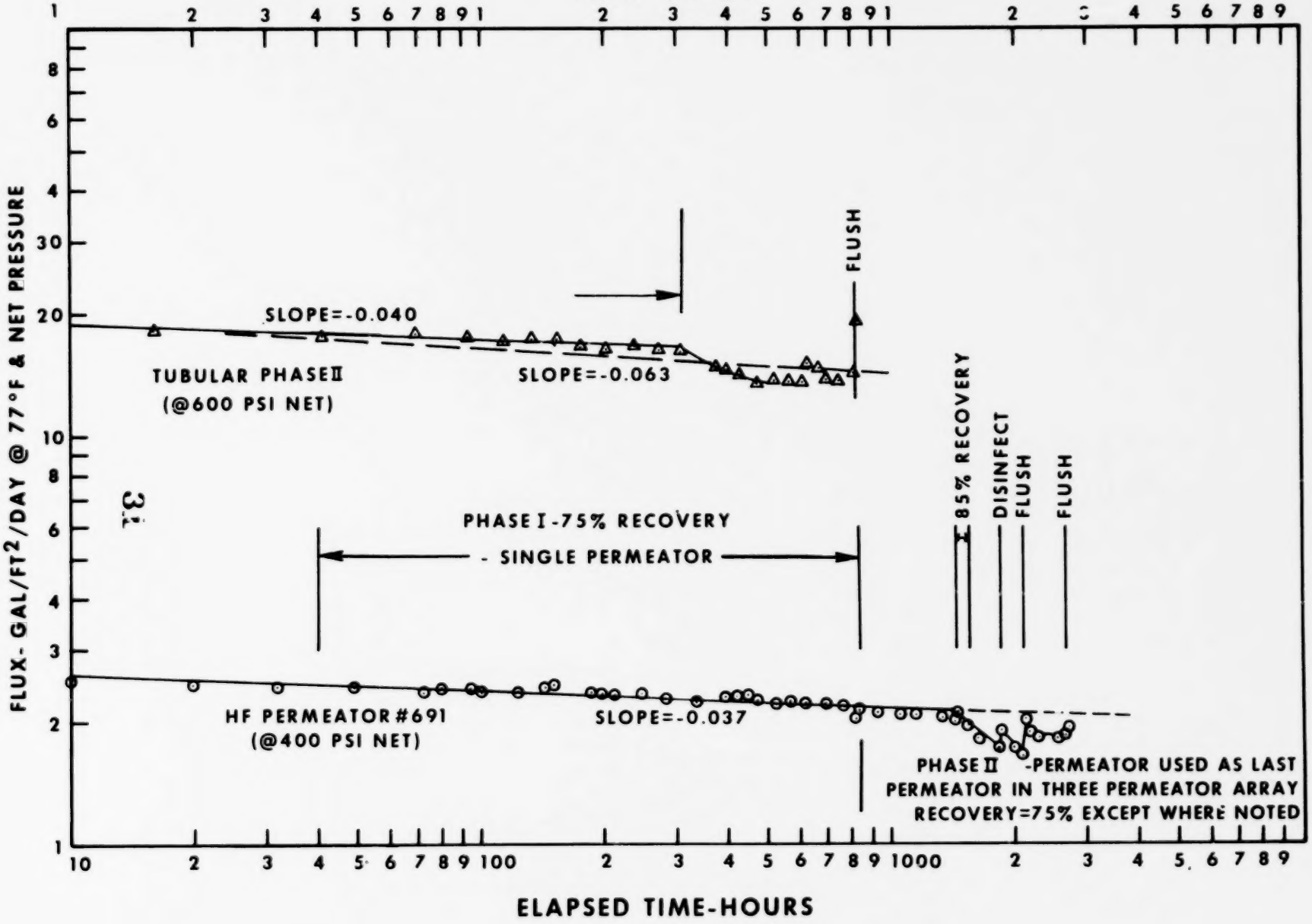


Table 11
Chemistry Analyses
Tubular Studies

Sample Designation	pH	Cond.	Acidity	Calcium	Magnesium	Total Iron	Ferrous Iron	Aluminum	Sulfate	TDS	Manganese	DO	Silica
Phase I @ 75 Percent Recovery													
Raw Feed	3.4	1050	250	125	92	78	61	12	660	1320*	14*	-	11*
Brine	3.1	2400	560	330	240	230	150	30	1650	3520*	39*	-	16*
Product	4.2	46	46	2.2	1.4	0.9	1.0	1.0	4.4	53*	0.31*	-	7.2*
Rejections		95.6%	81.6%	98.2%	98.5%	98.8%	98.4%	91.7%	99.3%	96.0%	97.8%	-	34.5%
Phase II @ 42.5 Percent Recovery													
Raw Feed*	3.4	-	-	110	83	70	63	8.3	800	1320	14	-	12
Brine*	3.1	-	-	200	150	130	160	15	1450	2300	25	-	21
Product*	4.3	-	-	0.6	0.45	0.4	0.62	0.15	2.0	25	0.08	-	1.0
Rejections	-	-	-	99.5%	99.5%	99.4%	99.0%	98.2%	99.8%	99.6%	99.4%	-	91.7%

$$\text{Rejections} = \frac{\text{Raw Feed} - \text{Product} \times 100}{\text{Raw Feed}}$$

*Asterisk denotes analyses by Rex Chainbelt
All other analyses by EPA

All units are mg/l except for pH and Specific Conductance (Micromhos/cm)

Table 12
Salt Passage
Tubular Studies

	Salt Passage - Percent	
	Type 310 Membrane Phase I	Type 610 Membrane Phase II
Calcium	1.45	0.43
Magnesium	1.11	0.36
Manganese	1.21	0.45
Total Iron	1.19	0.45
Aluminum	1.40	0.39
Silica	53.6	5.88
TDS	2.34	0.87
Ferrous Iron	1.15	0.51
Sulfate	1.27	0.20

Analyses by Rex Chainbelt

Note: Salt passage is related to salt rejection. Whereas rejection measures a membrane's impermeability to passage of ions, salt passage is a measure of the relative permeability to passage of ions. Therefore salt rejection plus salt passage equals 100 percent if both are measured in respect to the same initial concentration.

Comparing the flux history of Phase I 310 modules to the flux history from the 1969 field testing,[1] significantly lower flux declines were noted in the present study. For example, greater than 80 percent of the original flux was lost in 400 hours in the previous study compared to about 45 percent of the original flux in the present study. This would indicate that the pretreatment system did have some effect on the tubular system operation.

For a more in-depth report of the hollow fiber and tubular studies at Mocanaqua, refer to Environmental Protection Agency Report Number 14010 FQR to be published in the spring of 1972.

DISCUSSION

In order to compare reverse osmosis systems, it was vital to make all comparisons on the same basis, i.e., under the same operating conditions. For this reason, water flux, when corrected for osmotic pressure (which corrects for water quality and recovery) and temperature, served as an effective unit for comparison of membrane performance. Water flux, however, did not compensate for efficient packaging of the membranes in the reverse osmosis system, and therefore was a poor basis for comparison of system performance.

For this paper, system performance was evaluated on the basis of Product Output per Cubic Foot of Vessel Volume per Unit of Time. To arrive at this factor, water flux was divided by pressure vessel volume.

Table 13 presents a summary of observed flux and productivity data from the Mocanaqua studies. Tubular and Phase I spiral wound data--although actual operation was at 600 psi--were also normalized to 400 psi to enable direct comparison with the hollow fiber unit.

In terms of average flux, spiral wound membranes were clearly superior with 400 psi fluxes of 12.3 gf^2d for spiral versus 10.40 for tubular and only 2.48 for hollow fiber.

However, as hollow fiber permeators pack from 8-10 times as much membrane in the same volume as the spiral system and 88 times as much as the tubular system (see Packing Density, Table 13), the low specific flux of the hollow fiber is made up for by greater membrane area. Although the hollow fiber flux rate ranged from only 12 percent to 20 percent that of the spiral system depending on the spiral's operating pressure, hollow fiber product output per cubic foot of vessel volume was from 2.2 to 3.3 times spiral output and from 14 to 21 times tubular output, again depending upon operating pressures.

The tubular system ranked lowest in both flux and output per cubic foot of vessel volume.

In Table 14, relative costs for each system are presented. Since a detailed cost analysis was beyond the scope of this paper, initial costs for purchase of one pressure vessel complete with membrane are used. Dividing the initial cost by the observed output (gallons per day of product) yielded the initial cost per unit output figures shown in the table. Although prices and relationships observed were valid for the Mocanaqua study, extrapolation

Table 13
Comparison of Water Production Capabilities

System	Pressure Vessel Volume ft^3	Enclosed Membrane Area ft^2	Membrane Packing Density ft^2/ft^3	Avg. Flux GFD^2 @ 77° F & 400 psi net	Total Vessel Flux per Day Gal/Day @ 77° F & 400 psi net	Output per Cubic Foot of Vessel Volume	
						per day @ 77°F & 400 psi net	per Min. @ 77°F & 400 psi net
				(19.28 @ 600)	(2892 @ 600)	(2559 @ 600)	(1.78 @ 600)
Spiral Wound (Phase I)	1.13	150	133	12.86	1929	1707	1.19
Spiral Wound (Phase II)	1.13	186	165	12.31	2290	2026	1.41
Hollow Fiber (Phase II)	0.65	1500	2308	2.48	3720	5723	3.97
Tubular (Phase II)	0.63	16.9	26.8	(15.60 @ 600) 10.40	(264 @ 600) 176	(418 @ 600) 280	(0.29 @ 600) 0.19

Table 14
Relative Cost

System	Cost for One Pressure Vessel and Membrane	Observed Output (Gal. per Vessel per day @ 77° F & Indicated Net Pressure)	Initial Cost per Unit Output (gal/day)
Spiral Wound Phase I	$ 850.[11]	2892 @ 600	$0.29
Spiral Wound Phase II	$ 850.[11]	2290 @ 400	$0.37
Hollow Fiber Phase II	$1000.[12]	3720 @ 400	$0.27
Tubular Phase II	$ 265.[13]	264 @ 600	$1.00

of these figures for large units would result in large errors. Other factors such as hardware requirements would vary with each application and manufacturer and were not included in pressure vessel-membrane package cost figures.

A third basis for comparison was product quality. Rejections were calculated by comparing the product concentration with concentrations entering the reverse osmosis unit. A summation of system rejections is presented in Table 15. Spiral wound membranes held a slight edge in rejecting ability.

The previously mentioned leaks during spiral wound Phase II studies were apparent in unit rejections, as seen in Table 15, but tube 3 rejections were of the same level as those from Phase I spiral studies.

Under Mocanaqua conditions, the rejection advantage of spiral membranes would be of little significance as product water from all three units would require additional treatment for pH, manganese, and iron before drinking water standards could be met.

The final and perhaps most important basis for comparison was the decrease of productivity with time as evaluated by log-log flux decline slopes. Table 16 includes several examples of log-log slopes as derived from Figures 10 and 12 and Table 13. In Table 16, the examples were chosen to simulate comparable recovery conditions. In all these examples, recoveries in the respective tubes or units were near or below 60 percent.

Phase II spiral wound again had a slight advantage in flux decline slope over the hollow fiber system. However, the hollow fiber slope was superior to Phase I spiral performance. The tubular system's slope, calculated from the line of best fit of the tubular log-log flux plot, was considerably steeper than either the spiral or hollow fiber slope.

Extrapolation of the flux curve to predict flux values at three years and five years was necessarily based on the assumption that the log-log flux decline slope remained constant. Validity of that assumption is certainly open to debate and only sustained operation over that period of time would prove or disprove it. If the assumption were valid, the flux levels at three and five years of elapsed time are given in Table 16.

Calcium Sulfate Fouling

Very little or no calcium sulfate fouling occurred at 75 percent recovery since the log-log flux plots had shallow slopes and were linear. However severe fouling observed at 85 percent recovery was due to calcium sulfate precipitation. Therefore, at some point between 75 and 85 percent recovery, the solubility of calcium sulfate was exceeded and precipitation occurred.

At 75 percent recovery, the brine was concentrated four times in relation to the raw feed; at 85 percent, the brine concentration was 6.67 times that of the raw feed. Using typical calcium and sulfate values from Table 1, Table 17 was generated.

Table 15
Comparison of Membrane Performance

System	Flux, Gal/Ft²/ Day @ 77° F & Indicated Pressure	Rejections[1], Percent									
		Conductivity	Acidity	Calcium	Magnesium	Total Iron	Ferrous Iron	Aluminum	Sulfate	Manganese	Silicon
Spiral Wound Phase I	19.28 @ 600	99.2	91.7	99.8	99.8	99.8	99.8	99.2	98.8	-	
Spiral Wound Phase II	12.31 @ 400	97.6	94.6	99.6	98.5	99.0	98.9	97.6	99.1	99.8	
Spiral Wound Tube 3, Phase II	11.58 @ 400	98.7	-	99.8	99.7	99.7	-	97.7	99.7	99.5	
Hollow Fiber Phase I	2.32 @ 400	-	-	99.5	99.3	99.2	99.1	97.8	99.7	99.4	95.1
Hollow Fiber Phase II	2.48 @ 400	96.9	84.8	99.2	98.8	98.9	98.9	94.7	99.5	-	-
Tubular Phase I		95.6	81.6	98.2	98.5	98.8	98.4	91.7	99.3	-	
Tubular Phase II	15.6 @ 600	96.2	-	99.5	99.5	99.4	99.0	98.2	96.9	99.4	90.0

[1]Rejection = (Conc. Influent - Conc. Product) x 100 ÷ Conc. Influent

Table 16
Projected Membrane Performance*

Unit	Flux @ 100 Hrs. (1)	Log-Log Flux Decline Slope	Predicted Flux After 3 Years	Predicted Flux After 5 Years
	$G/ft^2/day$			
Spiral Wound Phase I Tube 1	21.5	-0.034	17.8	17.5
Spiral Wound Phase II Tube 1	13.0	-0.012	12.2	12.1
Hollow Fiber Phase II Tube 1	2.9	-0.015	2.7	2.6
Tubular Phase II Unit	17.2	-0.063	12.1	11.7

*Assumptions:

a. Log-log flux decline slope remains constant
b. Salt rejection is assumed to remain constant

(1) Taken from log-log graph of flux versus time

Table 17
Calcium Sulfate Molar Solubility Products

Recovery	Concentration Factor	Raw Feed Calcium mg/l	Raw Feed Sulfate mg/l	Brine Calcium mg/l	Brine Sulfate mg/l	Molar Solubility Product
75%	4.	120	800	480	1920	24×10^{-5}
80%	5.	120	800	600	3000	47×10^{-5}
85%	6.67	120	800	800	5340	111×10^{-5}

As shown in Table 17, the product of molar concentrations[4] of calcium and sulfate in the brine varied from 24×10^{-5} to 111×10^{-5} as the recovery was increased from 75 to 85 percent.

Since no $CaSO_4$ precipitation occurred at 75 percent recovery, the limiting concentration was in excess of 24×10^{-5}. If the point of precipitation were midway between 75 and 85 percent recovery, this would correspond to a solubility product near 50×10^{-5}. It is felt that precipitation occurred in the solubility product range of $35 - 50 \times 10^{-5}$.

ACKNOWLEDGEMENTS

The authors wish to thank the following persons for their willing assistance in bringing this study to a fruitful conclusion: J. E. Milanowski and R. E. Wullschleger, Rex Chainbelt, Milwaukee, Wisconsin; Ronald D. Hill, Environmental Protection Agency, Cincinnati, Ohio; Robert B. Scott, James L. Kennedy, Roger A. Dean, Howard W. Howell, and Maxine Cooper, Environmental Protection Agency, Norton, West Virginia; James L. Sleigh and Seymour Kremen, Gulf Environmental Systems, San Diego, California; Victor J. Tomsic, E. I. DuPont de Nemours, Wilmington, Delaware; Calgon-Havens Company, Pittsburgh, Pennsylvania, and David Maneval and John Buscavage, Commonwealth of Pennsylvania, Harrisburg, Pennsylvania.

Special thanks to J. Randolph Lipscomb and Alvin W. Irons of EPA, Frank Toman of Rex Chainbelt, and Frank S. Dilliplane of West End Coal Pockets, Mocanaqua, Pennsylvania.

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